

## Electrochemically Deposited Films of Bismuth Telluride and Related Materials for Thermoelectric Device Application..

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$\text{Bi}_2\text{Te}_3$  is a material that has been used for thermoelectric cooling, and this compound and related compositions are considered to be among the best materials available for such applications [1]. Electrochemical deposition of compound semiconductors is a field that has grown considerably in recent years, primarily with applications to solar cells or optoelectronic devices [2]; application of this technique to fabrication of films of  $\text{Bi}_2\text{Te}_3$  for thermoelectric devices follows logically from that work. Electrochemical deposition of  $\text{Bi}_2\text{Te}_3$  has recently been demonstrated [3,4]. This paper presents a study of deposition conditions and substrates for fabrication of thin films of  $\text{Bi}_2\text{Te}_3$  and related ternary solid solutions of  $\text{Bi}_{(2-x)}\text{Te}_{(3-x)}\text{Se}_x$  and  $\text{Bi}_{(2-x)}\text{Sb}_x\text{Te}_{(3-x)}$ .

$\text{Bi}_2\text{Te}_3$  has been deposited potentiostatically from acidic, aqueous solutions of  $\text{BiO}^+$  and  $\text{HTeO}_2^+$  on a variety of substrates. We have studied the effect of electrolyte composition, and of deposition potential and current density on composition and grain size of  $\text{Bi}_2\text{Te}_3$  films, as well as the effect of different substrate materials. It has been found that the best surface for  $\text{Bi}_2\text{Te}_3$  deposition with anti adhesion is noble metals such as Pt or Pd. These metals may be sputter or electrochemically deposited on a conducting or non-conducting substrate. Films have been deposited from  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4/\text{HCl}$  solutions; different acids were used to avoid substrate dissolution. It was found that the best deposits were made from  $\text{HNO}_3$  solutions. Composition may be varied by changing the relative ratio of  $\text{BiO}^+$  and  $\text{HTeO}_2^+$  in solution and by changing the deposition potential and/or current density during deposition. Grain size of the film is dependent on the growth rate, which is in turn, dependent on the current density during deposition. Films ranging in thickness from 500 Å. to several microns

$\text{Bi}_2\text{Te}_3$  may be deposited as Te-rich or Bi-rich films. This study has found that there is an effect of Bi/Te ratio in the solution, but that deposition potential is the major factor in controlling the composition in deposited films. Bi-rich films may be a combination of  $\text{Bi}_2\text{Te}_3$  and  $\text{BiTe}$ . Te-rich films may contain some elemental Te. The films are polycrystalline with some preferential orientation. The degree of orientation appears to be related to grain size. It has also been shown that ternary compositions of  $\text{BiTeSe}$  and  $\text{BiSbTe}$  can also be deposited electrochemically from acidic solutions containing all constituents.

Electrodeposited films have been characterized by optical and electron microscopy including microprobe analysis and X-ray diffraction. Characterization of electrical and thermoelectric properties of the films is in progress. Applications of these films will be discussed.

## REFERENCES

1. J. Goldsmid, *Electronic Refrigeration*, Pion Ltd., London (1986).
2. R. K. Pandey, S. N. Sahu, S. Chandra *Handbook of Semiconductor Electrodeposition*, Marcel Dekker, 1996
3. M. Takahashi, Y. Katou, K. Nagata and S. Furuta, *Thin Solid Films*, 240(1-2), 70(1994).
4. P. Magri, C. Boulanger and J.M. Lecuire in *Proc. XIII Intl. Conf. on Thermoelectrics*, B. Mathipraksam, ed., Part I (1994).

## REFERENCES

- 1 N. Weber, *Energy Conv.*, **14**, 1 (1974).
2. T. Cole, *Science*, **221**, 915 (1983),
3. C.P. Bankston, "T. Cole, R. Jones and R. Ewell, *J. Energy*, **7**, 442 (1983).
4. M.A. Ryan, B. Jeffries-Nakamura, R.M. Williams., M.L. Underwood, D. O'Connor and S. Kikkert, *Proc 27th IECCE*, **3**, 7 (1992).
5. M.A. Ryan, B. Jeffries-Nakamura, D. O'Connor, M.L. Underwood and R.M. Williams, *Proc. of Symp. on High Temp. Electrode Mat.*, ECS, **91-6**, 11 S (1991),
6. M.A. Ryan, A. Kisor, R. M. Williams, B. Jeffries-Nakamura, and D. O'Connor; *Proc. 29th IECCE*, **2**, 877 (1994),
- 7 J.R. McBride, D.J. Schmatz, T.K. Hunt and R.F. Novak, *Proc. 2nd Symp. Electrode Materials and Processes for Energy Conv. and Storage*, Electrochemical Society, **87-12**, 594 (1987),
8. M. L. Underwood, R. M. Williams, B. Jeffries-Nakamura, C. P. Bankston, N. Weber, and G. Harkins, Abstract #20, 175th ECS, May 1989.
9. 11, Nakata, T. Nagata, K. Tsuchida and A. Kato; *Appl Electrochem.*, **23**(12), 1251 (1993)
10. (a) C. Herring, *J. Appl. Physics*, **21**, 301 (1950).  
(b) V.T. Binh & R. Uzan, *Surf. Sci.*, **179**, 540 (1987)
11. M.A. Ryan, R.M. Williams, C. Saipetch, A. Kisor, D. O'Connor, M.L. Underwood and B. Jeffries-Nakamura, *Proc. 11th Symp. on Space Nuclear Power and Propulsion*, M. S. El-Ghenk and M.D. Hoover, eds., AIP, (1994).
- 12, R.K. Sievers, T.K. Hunt, J.F. Ivanenko and M.J. Schuller, *Proc. 28th IECCE*, **1**, S43 (1993).